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Corrosion of Iron and Steel

IT is a difficult task for any one man to review the present state of knowledge of such a wide subject as the corrosion of iron and steel, because he can only have direct experience of a limited number of its branches. He has to rely on a study of the literature for his knowledge of the remainder, and it is not always easy to assess the literature at its true value. For example, anyone not directly associated with the production and use of rust-resisting steels would find it difficult to decide on the practical significance of a research on the intercrystalline corrosion of austenitic chromium-nickel steels. This is the weakness of an article by Dr. Franz Eisenstecken[1] that has recently appeared in *Stahl und Eisen* under the title "Present State of Knowledge of the Corrosion of Iron and Steel and their Protection Against Corrosion."

This criticism would not have arisen had the author chosen a different title for his paper, such as "Some Recent Researches on the Corrosion of Iron and Steel," for, as he himself states in the text, it is really a survey of researches on the corrosion of iron and steel and their protection against corrosion published during the past few years. As such, his article can be commended to the reader as a useful critical summary of directions in which progress in these fields has been made or is being attempted. It should be emphasised, however, that whilst many of the statements quoted by Dr. Eisenstecken may be accepted as facts or "knowledge," others cannot be regarded as being more than interesting possibilities. Moreover, the list of references given by Dr. Eisenstecken, although amounting to 180, is far from complete. He seems to be unfamiliar with several important British papers, for instance, and the reader wishing to have a more complete critical bibliography might usefully consult papers by T. P. Hoar[2] and J. C. Hudson,[3] in addition to the one under review. It may be added that the main subjects discussed by Dr. Eisenstecken are modern theories of corrosion, the effect of the surface condition, and of the composition of the material, including sections on the influence of deformation or welding and the corrosion of rust-resisting steels, the effect of service conditions, in which considerable attention is paid to soil corrosion and corrosion in hot water plants and steam generators, protection by metallic and non-metallic coatings and laboratory methods of testing.

It may be of interest to devote the remainder of this review to a brief statement of knowledge of the corrosion of iron and steel in a few general fields of service. This statement will be confined to the corrosion of the ordinary ferrous materials used for structural work, as distinct from high-alloy steels.

THE CORROSION OF BARE IRON AND STEEL

Atmospheric Corrosion.—(*a*) The rate of corrosion of unprotected commercial irons and steels in the open air is known to vary from practically nil in dry tropical atmospheres to rates of the order of 0·005in. per year (equivalent to 3·3 oz. per square foot per year) in industrial atmospheres. The rate of rusting is essentially determined by the pollution of the atmosphere, provided that the humidity and rainfall are adequate for the corrosion process, so that general corrosion is not usually excessive in humid tropical atmospheres free from pollution by smoke, although pitting may occur under these circumstances.

(*b*) There is evidence that, under normal conditions, the rate of general rusting decreases with time, although, under some circumstances, the presence of scaly rust on bare iron and steel may lead to a marked local increase in the rate of attack.

(*c*) Of the three types of wrought ferrous materials, wrought iron containing appreciable quantities of slag (total phosphorus and silicon contents of the order of 0·35 per cent.) is approximately 20 per cent. more resistant to atmospheric attack than ordinary mild steel, whereas ingot iron corrodes at approximately the same rate as mild steel. The purest wrought irons, with a low slag content (total phosphorus and silicon about 0·07 per cent.) are, however, more corrodible than ordinary mild steel.

(*d*) It has been established that certain low-alloy steels are considerably more resistant to rusting than ordinary steel. The earliest steel of this type, containing 0·2 per cent. of copper or more, may be regarded as being 25 per cent. more resistant than the unalloyed steel. The addition of small percentages of chromium to these copper-bearing steels results in a further increase in resistance up to, say, 40 per cent. More sweeping claims have been made in America for low-alloy steels containing phosphorus and silicon in addition to copper and chromium. Although these claims have not, as yet, been confirmed in this country, it does not necessarily follow that the American results are wrong. In the first place, they are based on tests over longer periods of exposure than have so far elapsed in this country, and it may be accepted that in the case of low-alloy steels of this type the rate of atmospheric corrosion tends to decrease with time. Secondly, we do not know the effect of the physical conditions of exposure on the relative behaviour of different materials. If steel A is twice as corrodible as steel B when they are exposed vertically, it does not follow that this will be the case when the steels are exposed horizontally or at an angle of 45 deg. Very few experiments have been conducted on this point, and although Professor G. Chaudron has recently reported the results of tests in which he determined the corrosion of separate faces of specimens exposed at various angles,[4] more extensive work is required to elucidate it. It may well be that the quantitative differences between the results of American work and of our own investigators are to be explained not only by the differences in the total periods of exposure, but also in the conditions under which the specimens were tested.

The net consequence of recent research in this field

is that there are now available to the structural engineer a range of low-alloy steels at a price not unduly in excess of that of plain carbon steel that are at least twice as resistant to atmospheric corrosion as the latter. For most practical purposes, however, it remains necessary to protect these steels against corrosion, so that it is doubtful whether full use can be made of their increased corrosion resistance in fields of service other than those in which steel is used bare or where the protective coating cannot be renewed. Indeed, there is still a very great gap between their behaviour and that of the rust-resisting steels, which are several thousand times more resistant to atmospheric corrosion than ordinary steel. Clearly, one of the objects of research must be to bridge this gap and to produce relatively inexpensive low-alloy steels that can be used for most general purposes without protection.

Marine Corrosion.—(*a*) As regards the development of low-alloy steels with increased resistance to rusting in sea water, although encouraging indications have been reported from time to time, it cannot be said that any advance has yet been made on ordinary steel in this respect. This statement does not necessarily apply to steel exposed to other marine conditions, such as a ship's superstructure, where the use of low-alloy steels of the copper-chromium and related types might prove advantageous.

(*b*) Despite the valuable work of the Institution of Civil Engineers, our knowledge of the quantitative aspects of marine corrosion is still lamentably meagre. In particular the effects of movement and of the possible formation of protective calcareous deposits from the sea water itself have not yet been adequately studied. The former is particularly important with regard to the corrosion of ships' plates, which form part of a large mass propelled at high speeds through the water. It is possible that these matters will be studied by the Marine Corrosion Sub-Committee of the Corrosion Committee of the Iron and Steel Institute and the British Iron and Steel Federation. A large series of immersion tests on commercial irons and steels recently begun by their French counterpart, the Commission de Corrosion de l'Office Technique pour l'Utilisation de l'Acier, should also yield valuable information concerning corrosion in sea water under stationary conditions.[5]

PROTECTIVE COATINGS

(*a*) The fundamental principles for the protection of iron and steel against atmospheric corrosion by painting have now been laid down in a clear and explicit manner and gained universal acceptance.[6] The iron or steel should first be descaled by pickling or sand blasting, not in general by weathering, which is a wasteful and unreliable process. The metal should be given one or two coats of an inhibitive primer, such as red lead, as soon as possible after descaling. There is considerable latitude in the choice of finishing coats, provided that these are of good quality. It is almost unnecessary to add that care should be taken that all painting is carried out by skilled labour under favourable climatic conditions.

(*b*) Considerable progress has been made in methods of descaling and treating steel surfaces before painting. In this connection reference may be made to the duplex process of pickling, introduced by Dr. H. B. Footner,[7] in which the material is first descaled in sulphuric acid and then given a final dip in a dilute bath of phosphoric acid. We may also anticipate developments in the use of inhibitive panel washes, containing phosphoric acid and chromates, for the surface treatment of existing iron and steel structures before painting.

(*c*) Metallic coatings are now being used to an increasing extent for the protection of structural steel work. Zinc has been the chief metal used so far, and experiments have shown that in the open air it is roughly fifteen times less corrodible than ordinary steel. Aluminium also yields very good service under many conditions and its use will undoubtedly be extended, as in all probability will be that of lead and tin, which are known to be several times more resistant to atmospheric corrosion than zinc. The extended use of these protective metallic coatings has been rendered possible by the development of the metal-spraying processes and by improvements in practical methods of electrodeposition. It is probable, too, that in certain fields of service the most economical method of protecting iron and steel will be found to lie in the combined use of metallic coatings and of paint.

CONCLUSION

Whatever our knowledge of the corrosion of iron and steel may be at the present moment, it is considerably greater than it was a few years ago, and it will certainly continue to increase at a rapid rate. The last decade has seen the formation of numerous national organisations similar to the Corrosion Committee of the Iron and Steel Institute and the British Iron and Steel Federation, all of whom are conducting researches into many aspects of the problem. Such Committees are now in existence in Belgium, France, Germany, Holland, and Sweden, whilst the *doyen* of them all, Committee A–5 of the American Society for Testing Materials, is still continuing its useful work in the United States. These Committees serve a very useful purpose, not only by obtaining new knowledge, but possibly to an even greater degree by ensuring the rapid dissemination of this knowledge within the industries concerned, with the result that technical progress does not lag behind scientific discoveries, as might otherwise be the case. It is certain that as a result of their activities our knowledge of the corrosion of metals will increase very rapidly.

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[7] H. B. Footner, "A Modern Method of Pickling Steel." First Report of the Protective Coatings Sub-Committee. Fifth Report of the Corrosion Committee, 1938, page 369. (The Iron and Steel Institute. Special Report No. 21.)

Metallic Conductivity

AN essential feature of the theory of the conduction of electricity in metals is that the electrons act as carriers of the electric charge. The supposition that all the electrons taking part can be treated as though they are molecules of an ideal gas resulted in initial successes in the study of the subject. The new theory which arose showed a connection between the electrical and thermal conductivity, known as the Wiedemann-Franz ratio, which was in general agree-

ment with facts. The relation between electrical resistance and temperature was less satisfying, and a theoretical temperature function, not liable to criticism, could not be evolved. A serious objection to this theory arose from considerations of specific heat; for example, if the electrons form a gas with an energy distribution according to Maxwell's law, energy must be supplied to electrons as well as to atoms when a metal is heated, and this would raise the specific heat by an amount which is not in accordance with the results of actual measurement. This difficulty was first removed in 1928 by Sommerfeld, who applied the new Fermi statistics to the electron gas instead of the Maxwell energy distribution. These methods took the quantum theory into account, and they led to new and more acceptable results.

In the meanwhile, the theory encountered difficulties as the result of the extension of experimental work down to very low temperatures. Observations of this kind led to the discovery that the resistance of all pure metals, free from stress, no longer proceeded in the customary linear relationship, but fell rapidly towards zero, provided that the temperatures were sufficiently low. The next theoretical step was a consideration of the motion of the free conductivity electrons, not as in a gas, but as in a periodic field of force of the same period as that of the atomic lattice. The big fall in resistance at low temperatures and its disappearance at T (abs.)=0, was explained as being due to the cessation of energy interchange between the electrons and the elastic waves of the lattice.

A good opportunity for those interested to become better acquainted with the phenomena of supraconductivity is offered by the recent publication of a book,[1] in which a clear and consistent account of the subject is given, without the detailed reference to all available experimental data which, though useful to the expert worker, tends to lack interest and to become confusing to the general scientific reader.

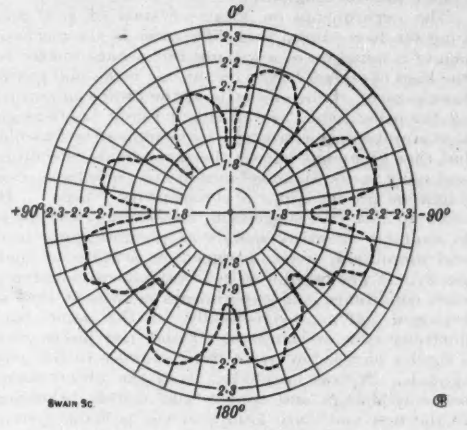
A further discovery showed that the electrical and thermal resistance depended on the crystallographic direction of the current in the case of metals, such as zinc, cadmium, &c., which do not crystallise in the regular system, and, further, that thermo-electric effects exist between samples of different crystallographic orientation though of the same metal.

Another experimental method adopted to provide an explanation of conductivity in metals was the exposure of the metal at different temperatures to an external magnetic field in order to divert the conducting electrons. Holding the view that the measurements of Kapitza and of Meissner and Scheffers, were an inconclusive test of the theory of the existence of a free electron gas, E. Justi and H. Scheffers[2] determined to carry out a series of resistance measurements for the purpose of extending the work of Meissner and Scheffers at the lowest temperatures and with higher field strengths.

The results of measurements carried out at 20 deg. and 14 deg. abs. on a crystal of pure gold showed that its resistance continually increased with the field strength, without any indication of reaching a maximum value. In order to confirm this basically important result, the measurements were repeated with a different arrangement each time, but in every case a linear rise was obtained at high field strengths, though with different inclinations of the curves showing the resistance plotted against the magnetic field. The only possible explanation for this difference was that the increase in resistance depended on the angles between the direction of the transverse magnetic field and the axes of the gold crystal. Further experiments actually showed that increase in resistance could be varied considerably by rotating the magnet about the gold rod as axis. Before it was possible to obtain reproducible polar diagrams of resistance in relation to magnetic field strength and crystal axes, it was necessary to develop a mounting for the crystal which would result in symmetrical rotation in respect of the applied field.

This newly discovered phenomenon of galvanomagnetic anisotropy in regularly crystallising metals showed that the metallic conductivity apparently was not the result of an isotropic electron gas, but of anisotropically bound electrons. This conclusion, however, could not be drawn from the known galvanomagnetic anisotropy of metals which do not crystallise in a regular system, since these have been shown to be electrically anisotropic without a magnetic field.

The measurement of the electrical resistance in



Relative Change in Resistance of a Gold Crystal Rotated in a Magnetic Field of 21·7 kG at 20·38 deg. abs.

magnetic fields for different crystallographic orientations now offers the possibility of examining the electrical anisotropy with a single test piece, whilst several test pieces of different crystal orientation are necessary when undertaking anisotropy measurements (without a magnetic field) in the case of metals not of a regular system. Measurements were carried out with crystals in the form of rods, whose axis (current direction) coincides with a specially low indexed direction, as, for example, the cube edge [100] or face diagonal [110] or space diagonal [111].

Polar diagrams of specially simple symmetry should be obtainable in such cases where the increase in resistance is actually determined by the crystal structure. The figure shows a polar diagram of the increase in resistance of a gold crystal rotated in a constant transverse field of 21·7 kG at T=20·38 deg. abs. The diagram must have at least four-fold symmetry, since the axis of the rod ran parallel to the cube edge [100]. Each time the field is normal to a cube face, a minimum appears in the increase of resistance. If the field strength is increased to 35,000 Gauss, then the anisotropy is still more noticeable, without its appearance being substantially altered. If, instead, the temperature is reduced from 20·38 deg. to 4·22 deg. abs. in order to "freeze-up" further the remaining lattice vibrations, then the so-called "anisotropy factor" is substantially increased, and

the polar diagram takes up a star-like appearance. Thus, better evidence than the polar diagram against the existence of an isotropic electron gas does not appear possible.

Attention was then paid to measurements on metals possessing different crystal structures, for the purpose of demonstrating that the mechanism of conduction varies according to the crystal structure and number of valency electrons, a result which would not be expected from an electron gas. Measurements were made on tungsten, a metal with body-centred cubic crystal structure (the form of greatest possible symmetry) of high chemical purity and great strength. The polar diagram of the resistance increase on swinging of a transverse field about the cube edge [100] showed, as expected, that here also the simplest symmetry relationships appear. The positions of the minima and maxima coincided exactly with those of the interferences in the Laue back-reflection diagram.

The experiments on single crystals of gold and tungsten have shown that differences in the mechanism of conduction at low temperatures are related to the kind of crystal lattice on the one hand, and to the arrangement of the electrons of the atoms concerned on the other hand. From this it might be assumed that a universal electron theory would not be feasible, but that all metals having the same crystal structure and lying in the same column of the periodic system might be grouped into a conductivity "type." In order to test this suggestion, an attempt was made to examine as many metals as possible; only lead and aluminium were examined in a state of high purity. It was possible to get molybdenum satisfying such conditions, and experiments confirmed that it belonged galvano-magnetically to the same conductivity type as tungsten. Copper test pieces gave a similar increase in transverse resistance to the gold crystals. It was concluded from the observations on molybdenum and copper that metals belonging to the first and sixth groups of the periodic system when of similar crystal structure at times possess identical conductivity types.

Some interesting observations were made as a result of an examination of aluminium of high purity. As expected, it could be confirmed in many ways that aluminium behaved differently from the first and sixth group metals examined; further, that aluminium possessed only a small anisotropy of the resistance increase, so that it could be described as electrically isotropic.

Experiments with lead crystals were made in order to find whether the different behaviour of aluminium was due to its place in the periodic system or whether it was because aluminium is supra-conducting compared with the metals of the first and sixth groups. Lead is also supra-conducting, besides being cubic face-centred, and belonging to the fourth group of the periodic system. It was shown that the electrical behaviour of the lead crystals cannot be included in the gold type, nor in the aluminium or the tungsten type, but represents a separately existing conductivity type. Thus the results with lead showed decisively that the supra-conducting property of aluminium was not related to its galvano-magnetic behaviour.

It is concluded that the tests on the electrical properties of metals of simple lattice structure showed that the theory of free electron gas cannot be applied to the mechanism of conduction. It was shown that each metal belongs, according to its crystal structure and valency, to one of a small number of conductivity types. Such investigations as to the origin of the electrical conductivity are naturally also of importance for the explanation of the conductivity of heat and of the mechanical anisotropy of the metals. It seems that a close relationship exists between the elastic and the electrical anisotropy. If the metals are arranged in order of increasing elastic anisotropy, a series is obtained beginning with aluminium and tungsten, through gold and copper, and finally leading to lead, which agrees with that obtained by arranging them according to their electrical anisotropy.

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A Polishing Machine for Micro-Sections

By ALAN BLAINEY, B. Eng., Department of Metallurgy, Liverpool University

IN the hand polishing of alloys of soft metals considerable difficulty is experienced in obtaining a surface free from scratches for micro-examination. This may be due to the use of an unsuitable polishing medium and/or excessive pressure between the specimen and the polishing cloth. To overcome this tendency to scratching and other disadvantages of hand polishing, a polishing machine has been evolved meeting the following requirements :—

(1) An even and light pressure to be exerted between specimens and polishing cloth.

(2) The specimens to be rotated during polishing as this gives better results.

(3) Provision to be made for the polishing of several specimens simultaneously.

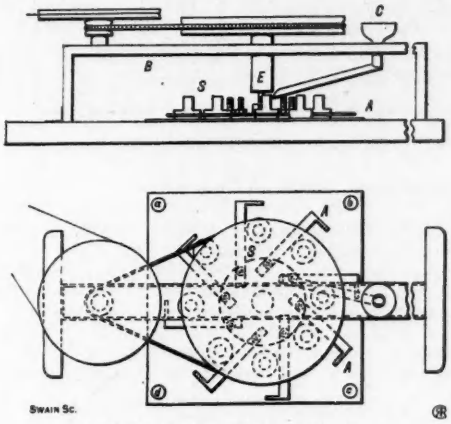
The use of a polishing wheel was rejected, as it would be difficult to arrange to polish several specimens at once and rotate them at the same time; further, the polishing medium tends to be thrown off the wheel by centrifugal force. It was therefore decided to use a fixed pad and to move the specimens over it.

The following form of machine has been devised and found to meet the requirements satisfactorily. It can be easily and cheaply constructed from the materials at hand in most laboratories. Referring to the diagram (Fig. 1) the machine consists of a bridge B made of channel-section brass carrying a bearing E and a cup C with a pipe for feeding oil on to the polishing cloths when necessary. The disc D carries eight arms A, and is rotated by a shaft passing through the bearing and driven by the pulleys above, power being obtained from a small motor. Pulleys are used in preference to gears as small metallic particles from the latter would fall on to the polishing cloth and scratch the specimens. The drive to the large pulley is a stout rubber band of the kind used for sealing tobacco tins. The specimens S are moved round by the arms, the latter being given a lead as shown so that a specimen will remain at the same distance from the end of the arm during rotation. In order to make the specimens rotate during polishing, the board on which the whole is mounted is tilted at an angle of about 10 deg., with the result that the specimens roll backwards and forwards along the arms as the latter move round. Thus, if the polishing surface slopes downward from *a b* to *c d*, the specimens move as shown in the

plan. The angle of lead of the arms and the tilt of the board are adjusted to suit the weight and size of the specimens and the nature of the polishing cloth.

The form of the specimens, which can be judged from the side view, enables them to be handled easily, and where additional pressure is required between specimen and cloth annular weights can be slipped over the necks. The specimens shown are cast in a specially prepared mould (though a simple cylindrical form would do just as well in most cases), and the end face is machined flat in a lathe. The machined faces of the specimens are hand ground on successively finer emery papers, finishing on Hubert 000 paper, paraffin being used as a lubricant to prevent dragging of the surface.

The specimens are now polished on Selvyt cloth with Brasso, the machine being used for this stage. The speed of rotation of the wheel is fairly high and the polishing cloth level, so that the specimens



Polishing Machine for Micro-Sections

are guided round at the ends of the spokes. It is arranged that polishing is in a direction at right angles to the scratches left by the last emery paper. The specimens are loaded with weights of about five times their own weight, and polishing continued until all the scratches are effaced (ten to fifteen minutes). The loading weights are then removed, the specimens turned round through 90 deg., and polishing continued for about five minutes.

After this the specimens are washed in petroleum ether to remove Brasso, and given a very short polish by hand on Selvyt with Silvo to remove Brasso particles which adhere to the surface. They are then ready for the final polish on Selvyt with a special emulsion of soap solution, paraffin oil, and freshly precipitated barium sulphate. This emulsion is prepared as follows :—

About one-sixth of a cake of Pears' Golden Glory soap is dissolved in 300 c.c. of hot water, 400–500 c.c. of filtered paraffin oil added, and the whole well shaken until the oil is emulsified. The barium sulphate is prepared by completely precipitating 100 c.c. of a saturated solution of barium chloride solution with sodium sulphate and washing six times with dust-free water, the volume being made up to 2 litres each time. The barium sulphate is then added to the emulsion and the whole well shaken at intervals during cooling. If the polish becomes too thick, it should be diluted with filtered paraffin oil.

On most alloys this polish gives a surface sufficiently free from scratches for high power work, provided the Selvyt is kept well supplied with emulsion.

This machine has only been used on soft alloys by the author, but has a wide range of application for all but very hard materials by increasing the pressure between specimen and polishing cloth, and the use of suitable polishing media.

The Sigma Phase in Iron-Nickel-Chromium Alloys

THE constitution of the carbon-free iron-nickel-chromium alloys was investigated in 1927 by E. C. Bain and W. E. Griffiths,[1] who studied about seventy alloys and produced diagrams indicating differences in constitution and structure, and the effect of heat treatment on alloys of different composition. In the course of this work they found that alloys containing approximately 30 to 55 per cent. of chromium with a small amount of nickel consisted of a hard, brittle constituent which they called B. It was formed from the α-solid solution by annealing at moderate temperatures (below 950 deg. Cent.). Later, F. Wever and W. Jellinghaus[2] showed that the brittle phase in question was a new phase of the iron-chromium system

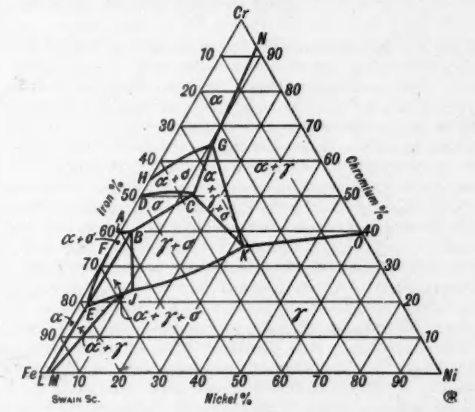


FIG. 1—*Iron-Nickel-Chromium Alloys; Isothermal Section at 800 deg. Cent.*

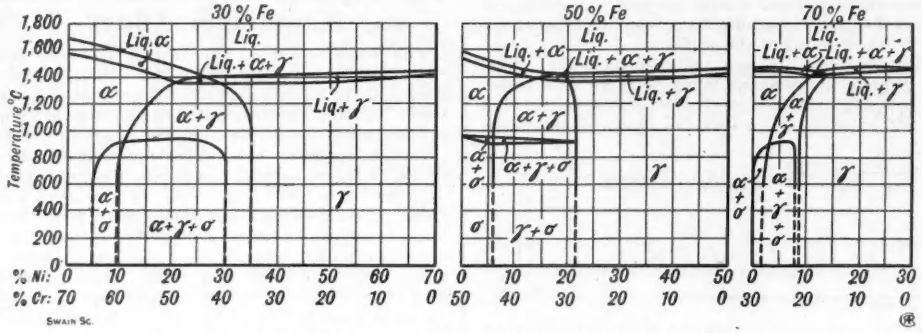
corresponding in composition to FeCr, dissolved in excess either of iron or of chromium. Its existence was confirmed by S. Eriksson,[3] who used X-ray methods. Wever and Jellinghaus produced a constitutional diagram of the iron-nickel-chromium alloys, but as they did not make use of prolonged annealing it does not represent true equilibrium. The diagram of Jenkins and his co-workers[4] should correspond very nearly to equilibrium conditions, as long periods of annealing were carried out, amounting in some cases to twenty-one days. In view of this, it is surprising that the brittle constituent—now known as the sigma phase—was not detected.

It has been the object of P. Schafmeister and R. Ergang[5] to study in detail the region of the iron-nickel-chromium diagram in which the σ phase appears. The matter is one of considerable technical, as well as scientific, interest as the precipitation

of the σ phase is known to produce marked embrittlement of the iron-chromium and iron-nickel-chromium alloys, though fortunately the change is so sluggish that it may very easily be suppressed.

Schafmeister and Ergang examined about fifty alloys made in the high-frequency furnace, and containing carbon 0·1 per cent. or less (in one case 0·14 per cent.), silicon about 0·3 per cent., and manganese 0·28 to 0·51 per cent. The alloys were annealed for two hours at 1200 deg. Cent., quenched in water, and, for the preparation of isothermal sections of the equilibrium diagram, annealed for 200 to 1000 hours at 800 deg. or 650 deg. Cent. The long annealing times are necessary as the precipitation of the σ phase is slow; on the other hand, they were found to be sufficient, since no important differences were observed between alloys annealed for 200 hours and those annealed for 1000 hours. The alloys were examined by microscopical, magnetic, and X-ray methods. As the σ phase is very hard its occurrence could also be established by hardness tests. From the data obtained two isothermal sections (at 650 deg. and 800 deg. Cent.), and three temperature-concentration sections at 30, 50, and 70 per cent. of iron were constructed. A comparison of the two isothermal sections revealed only small differences between the phase boundaries at 800 deg. and at 650 deg. Cent., thus indicating the probability that any further changes down to room temperature are likely to be small. Only the 800 deg. isothermal section (Fig. 1) is reproduced here, together with the sections across the diagram at 30, 50, and 70 per cent. of iron (Figs. 2 to 4). The paper contains drawings of the solid model, from which it is seen that the σ region is in the form of a "tunnel" or cave, the walls of which are α+σ and γ+σ and the roof α+γ. The "entrance" is on the iron-chromium boundary, and as the tunnel penetrates the ternary region, its width after a short parallel section, rapidly narrows down to vanishing point.

Any alloy in the region A B C D (Fig. 1) is completely converted into the brittle σ phase by prolonged annealing at temperatures below about 920 deg. Cent., the maximum solubility of nickel in the σ phase being about 10 per cent. Any alloy which lies within the region F E J K G H F is liable, with similar treatment, to precipitate the σ phase, and so become more or less embrittled. The limits within which precipitation occurs will naturally be displaced by differences in composition. For example, whereas an alloy containing nickel 20 per cent. and chromium 25 per cent., with 0·3 per cent. of silicon showed no precipitation after being annealed for 1000 hours at 800 deg. Cent., the corresponding alloy with 3 per cent. of silicon showed marked precipitation after the same treatment. This result is in agreement with the conclusions of A. G. H. Anderson and E. R. Jette,[6] who found, in their work on the iron-chromium-silicon diagram, that the region in which the σ phase was stable was extended to a lower chromium content by the addition of silicon. On the other hand, it was found that variation in carbon content, such as may occur in commercial alloys (*i.e.*, up to about 0·3 per cent.) was without influence.



FIGS. 2 TO 4—*Sections Across the Iron-Nickel-Chromium Equilibrium Diagram*

For the details of how each line on the diagram has been determined, reference must be made to the original paper, but it is of interest to note the differences in hardness characteristic of the different phase fields. Fig. 5 shows the hardness of a series of alloys containing 20 per cent. of nickel with increasing amounts of chromium. Beyond 25 per cent. of chromium the hardness of the quenched (α+γ) alloys goes up with increase of chromium content. This is due to partial breakdown of a supersaturated solid solution. On annealing, the high chromium alloys are softened on account of coalescence of the precipitated particles. From 25 per cent. of chromium, where the composition crosses the line J K (Fig. 1) up to 40 or 48 per cent., they are hardened, owing to the separation of the σ phase.

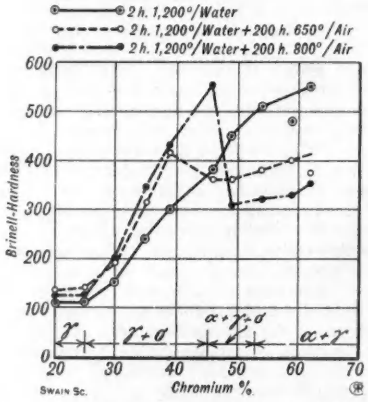


FIG. 5—*Hardness of Alloys Containing 20 per Cent. of Nickel, After Different Heat Treatments*

The temperature of reheating required to convert the σ phase back into the α-solid solution was not accurately determined, but lay in the region of 900 deg. to 1000 deg. Cent. The change was followed in two alloys, one just within and the other well within the γ+σ region J K C B. The specimens which had been annealed for 200 hours at 800 deg. Cent. were reheated for half an hour at 50 deg. intervals between 850 and 1050 deg. Cent. The hardness and magnetic tests, represented in Fig. 6, show that in the 30 : 20 chromium-nickel alloy, the

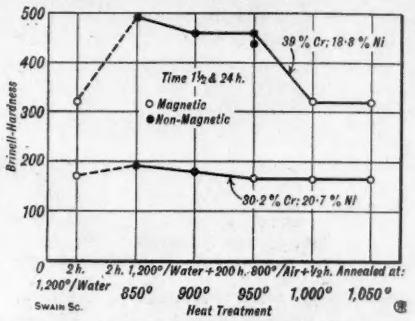


FIG. 6—*Effect of Annealing Temperature on Hardness and Magnetic Condition of Two Alloys*

change was complete at 950 deg., while in the 39 : 19 chromium-nickel alloy it had not occurred at that temperature even after twenty-four hours, but was complete at 1000 deg. Cent.

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The Electrolytic Polishing of Iron and Steel

THE electrolytic polishing of copper, aluminium, tin, and of certain alloys has been described by Jacquet.[1] The method has been applied to zinc,[2] to cobalt,[3] and to nickel.[4] It has now been extended by P. Jacquet and P. Rocquet[5] to the polishing of iron and steel for microscopic examination. Their object was to simplify the somewhat long and delicate operation of metallographic polishing and to avoid the formation of any deformed surface layer. The electrolyte employed was made by pouring slowly, a little at a time, 765 c.c. of pure acetic anhydride into a cooled vessel containing 185 c.c. of 65 per cent. perchloric acid (density 1·61), and then adding 50 c.c. of distilled water. The mixture should be prepared at least twenty-four hours before it is to be employed, and if, after long use, it becomes less effective it can be regenerated by small additions of water (about 1 per cent.). The specimen, whose surface has been freed from all foreign matter by abrasion, forms the anode. The cathode may be a plate of iron or of aluminium. The current density should be between 4 and 6 amperes per square decimeter of anode surface. During electrolysis the temperature must not exceed 30 deg. Cent.; hence the electrolytic cell must be kept cool. The solution should be agitated, and since its resistance is high, direct current at a voltage of at least 50 volts is required. In these circumstances, microscopic polishing of a surface previously prepared with 000 emery paper takes about four or five minutes. If the specimen has been finished on coarser emery or has been rubbed on a file, a considerably longer time is taken. When the specimen is taken out of the bath it is covered with a viscous brownish-red layer, which is easily removed by washing in a current of water followed by rinsing in distilled water and in alcohol. In general, the structure of the steel is only very slightly revealed by the anodic treatment, and subsequent etching with the usual reagents is necessary. Jacquet and Rocquet have polished, by this means, a variety of annealed and heat-treated steels of a wide range of carbon content, showing martensitic, sorbitic, and pearlitic structures. White cast iron can be treated, but not iron containing graphite.

The theory of electrolytic polishing is not completely understood. The reddish-brown surface layer surrounding the anode, in which the products of attack accumulate, and which appears to play an essential part in the process of polishing, is thought to contain the complex salt

$$[Fe_3Ac_6(OH)_2]\,ClO_4.\,4\,H_2O,$$

which is known to be very soluble in concentrated acetic acid. The iron dissolved from the anode per minute at a current density of 1 ampere per square decimetre was found to be 16 milligrams, while the theoretical amount of ferrous ion formed under these conditions would be 17·8 milligrams. It is probable that the perchloric ions contribute to the oxidation of the ferrous ions in the vicinity of the anode and facilitate the formation of the aceto-ferric ion.

For different types of steel some modification of the electrolyte is said to be desirable. For example, nickel and nickel-chromium austenitic steels can be polished in the solution already described at a current density of at least 10 amperes per square decimetre, but it is preferable to use a solution containing 665 c.c. of acetic anhydride and 335 c.c. of 65 per cent. perchloric acid, at a current density of about 6 amperes per square decimetre. This solution also serves well for 3 per cent. silicon steel. For carbon steel the first solution mentioned above may be modified by dissolving in it, by anodic attack, about 0·5 per cent. of aluminium. This produces an increase of viscosity, and more energetic agitation may be used with a current density of 3 amperes per square decimetre.

In general, electrolytic polishing of steels is very rapid after a certain experience of the method has been acquired. Specimens of any form and dimensions may be polished on all their faces. The attack of etching reagents is much more active on an electrolytically polished surface than on the same alloys polished mechanically, and a better contrast is obtained between the constituents. Moreover, non-metallic inclusions and flaws are more clearly defined and suffer less risk of damage than in surfaces produced by mechanical polishing.

Further experimental details promised by the authors will be awaited with interest, as it appears that the method may have important applications.

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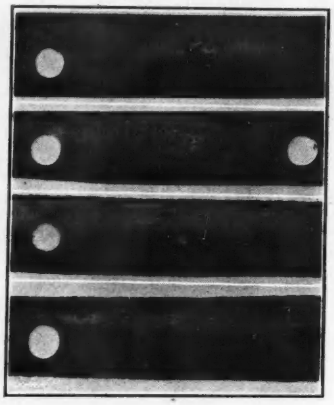
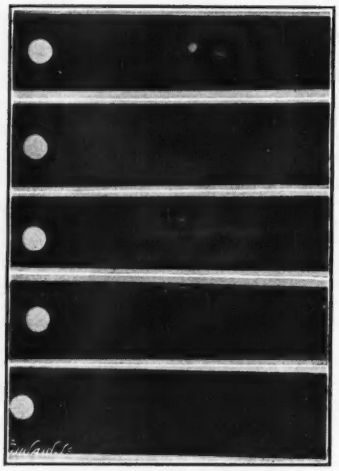


GROUP I

Material.	Appearance of surface under jet.	Loss of thickness under jet.
		in.
Arsenical brass	Severe local attack	0·014
70/30 brass	Severe local attack	0·015
70/30 cupro nickel	Some local attack	0·005
10 per cent. tin-bronze ...	No local attack	0·001



GROUP II

Material.	Appearance of surface under jet.	Loss of thickness under jet.
		in.
70/30 brass	Severe local attack	0·047
70/30 cupro nickel...	Some local attack	0·008
10 per cent. tin-bronze... ...	No local attack	0·0006
12 per cent. tin-bronze... ...	No local attack	0·0004
14 per cent. tin-bronze... ...	No local attack	0·0004

New Alloy Condenser Tubes*

ALTHOUGH bronze has been accepted as one of the most valuable corrosion-resisting metals available to engineers, the difficulty in making thin-walled tubes has in the past prevented its commercial use for condenser tubes. Recent improvements in the degasification of molten bronze have greatly diminished these difficulties, and tin-rich bronzes containing 10 per cent. of tin have now been fabricated into condenser tubes and are in service in the main condenser of a large electric power station.

A practical trial of this kind must run for many months or even years before conclusive results are available and accelerated trials have therefore been carried through.

Groups of samples were tested on the lines developed by the Corrosion Research Committee of the Institute of Metals over a period of years, which have been proved to give results accurately paralleled by industrial installations.

* Contributed by the International Tin Research and Development Council.

TWO TYPES OF CORROSION

Two types of tests are made, namely, "jet impingement" and "sediment corrosion." The first is representative of modern high-duty condensers where the water velocity is so high that a scouring action prevails and bubbles of entrapped air impinge on the tube walls. The second test represents conditions where water velocity is lower and where a sediment is deposited inside the tubes. The types of corrosion arising under these conditions are entirely distinct, and while some condenser tube metals are comparatively resistant to one type of attack, they are comparatively vulnerable to the other.

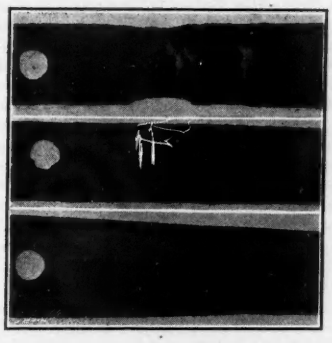
The object of the tests was to compare the merits of bronzes, containing 10, 12, and 14 per cent. of tin, with the alloys now in common use for condenser tubes.

Groups of specimens of various alloys were tested simultaneously, the water used was sea water, and in some tests it was known to contain bacteria which

promote corrosion, in other tests such bacteria were absent.

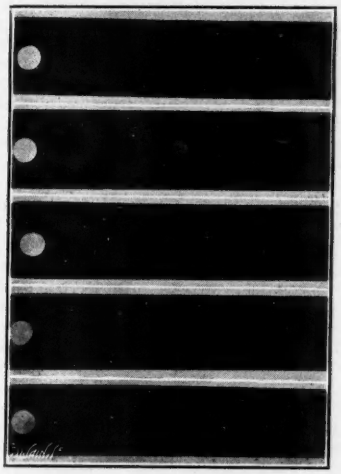
Within the range of accuracy of such tests it has been demonstrated that bronze condenser tubes show outstanding resistance to jet impingement and bacterial attack, and in this, as well as in the series of "sediment" tests, have proved equal or superior to the best tubes at present in use.

It is also demonstrated that about 10 per cent. tin is sufficient to give these results, and, bearing in mind the relative costs of the various metals, this alloy provides a remarkably attractive condenser tube.



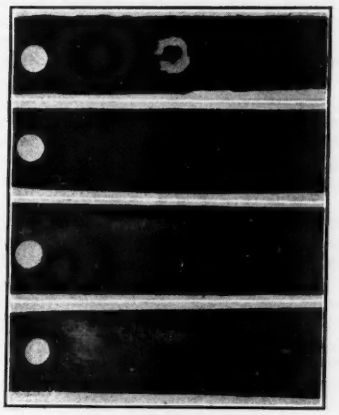
GROUP III

Material.	Appearance of surface under jet.	Loss of thickness under jet. in.
70/30 brass	Extensive attack	0·036
70/30 cupro nickel...	Severe attack	0·009
12½ per cent. tin-bronze... ...	No local attack	nil



GROUP IV

Material.	Appearance of surface under jet.	Loss of thickness under jet. in.
70/30 brass	Severe local attack	0·029
2 per cent. aluminium-brass...	Slight local attack	0·0012
70/30 cupro nickel	Considerable local attack ...	0·012
10 per cent. tin-bronze ...	No local attack	0·0004
14 per cent. tin-bronze ...	Some local attack...	0·002



GROUP V

Material.	Appearance of surface under jet.	Loss of thickness under jet. in.
70/30 brass	Heavily perforated	0·048
70/30 cupro nickel	Slight local attack	0·0125
12½ per cent. tin-bronze ...	No local attack	0·002
14 per cent. tin-bronze ...	No local attack	0·0005

Advances in Microscopy

THE purpose of this article is to draw attention to some recent advances in the art of microscopy and in particular to give some account of the electron microscope and its application to the study of metals. It is almost impossible to approach this subject without some consideration of the question of the resolving power of the instrument. The theory of Abbe is so well known that we need only state the result, namely, that if the rulings of a grating are to be visible in a microscope their interval must exceed one-half the wavelength of the light employed, this wavelength being reckoned in the medium between the object and the lens. In symbols, if μ is the refractive index of the medium and if λ is the wavelength of the light *in vacuo*, then the interval e of the grating which can just be resolved is :

$$e = \lambda/2\,\mu \sin\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

α is the semi-vertical angle of the cone of light rays grasped by the objective, and for high-power lenses is so nearly 90 deg. that we may put $\sin\alpha = 1$ for our present purposes. Numerically, we have for visible light $\lambda = 5500$ A.*, and μ is usually assumed to be about 1·60, so that the closest interval that can be seen is about $0{\cdot}17 \times 10^{-3}$ mm. To render this interval visible a magnification of 1000 diameters should be sufficient, as this will separate the centres of neighbouring rulings by 0·17 mm., a distance within the resolving power of the eye ; but for convenience of observation a magnification of 1500 might be used. So far as an object with a periodic structure, such as a grating, is concerned, it is certain that an observer with good eyesight should be able to see all that there is to be seen in the image under a magnification of 1000 diameters. It should be observed that this conclusion refers only to objects having a periodic structure ; such structures are not infrequently the subject of microscopical investigation, the lamellæ in pearlite being a familiar example in metallography, a fact which, to some extent, lessens the artificiality of the grating as the test object of the physical theory. The failure to appreciate the significance of the nature of object observed has led to a considerable amount of misunderstanding of the meaning of the terms "resolving power" and "limit of resolution." Commenting on this the late Lord Rayleigh[1] has made some observations which it seems desirable to quote. He writes : "The importance of the general conclusions above formulated, as imposing a limit on our powers of direct observation, can hardly be overestimated ; but there has been in some quarters a tendency to ascribe to it a more precise character than it can bear, or even to mistake its meaning altogether. . . . The first point to be emphasised is that nothing whatever has been said as to the smallness of a single object that may be made visible. The eye unaided, or armed with a telescope, is able to see, as points of light, stars subtending no sensible angle. The visibility of a star is a question of brightness simply and has nothing to do with resolving power. The latter element enters only when it is a question of recognising the duplicity of a double star, or of distinguishing detail on the surface of a planet. So in the microscope there is nothing except lack of light to hinder the visibility of an object, however small. But if its dimensions be much less than the half wavelength, it can only be seen as a whole, and its parts cannot be distinctly separated, although in cases near the border line some inference may be possible, founded on experience of what appearances are presented in various cases." The difference here emphasised between the visibility of an object and the resolving power of the instrument is so important that it is worth while continuing to quote from the same source a simple experimental demonstration of the fact that a dark linear interruption of a bright background may be visible, although its width is much less than a half wavelength. "In front of the naked eye was held a piece of copper foil perforated by a fine needle hole. Observed through this the structure of a wire gauze just disappeared at a distance from the eye of 17in., the gauze containing forty-six meshes to the inch. On the other hand, a single wire, 0·034in. in diameter, remained fairly visible up to a distance of 20ft. The ratio between the limiting angles subtended by the periodic structure of the gauze and the diameter of the wire was $(0{\cdot}022/0{\cdot}034) \times (240/17) = 9{\cdot}1$."

In recent years some interesting work has been done on the use of optical microscopes of high resolving power. Wrighton[2] in 1933 described experiments with an objective by which a pearlitic structure in steel, consisting of lamellæ occurring with a frequency of 160,000 to the inch, was clearly resolved. In places the structure consisted of a few lines separated by only 1/200,000th of an inch. A magnification of 2500 and a wavelength of 4400 A were employed. The theoretically possible resolution appears to have been achieved. Lucas[3] in 1934 published results obtained with a quartz objective designed for use with ultra-violet light ; magnification of 4000 diameters was used and the improved resolution of carbide particles in a steel was demonstrated. More recently Smiles and Wrighton[4] (1937) have compared the performance of two objectives, one for use in the visual region $\lambda = 4400$ A, of numerical aperture 1·6, the other a quartz objective for use with ultra-violet light $\lambda = 2750$ of numerical aperature 1·25. The equivalent aperture of the latter is 25 per cent. greater than that of the former owing to the shortness of the wavelength employed. A number of different metallurgical specimens was examined at magnifications up to 2500 diameters, and it was concluded that the results obtained with the quartz objective were the better. Whether the improved resolving power is sufficient reward for the additional difficulties inherent in the use of ultra-violet light seems to be an open question.

It would be rash to say that no further advances in the direction of higher resolving power, which would justify the use of larger magnifications, are possible for the optical microscope. Nevertheless, the work described above suggests that the limit is being approached even if it has not been attained. The resolving power is determined by three factors : (i) The angular grasp of the objective which is nearly 180 deg. its geometrical limit ; (ii) the refractive index of the medium between the object and the lens, which at 1·60 is not susceptible of any large increase ; and (iii) the wavelength of the light employed. It is under this last heading that some improvement may be possible ; but it seems unlikely that the resolution attainable can be more than doubled.

Passing down the scale of wavelengths of known types of radiation, we come next to X-rays having wavelengths of the order of one-thousandth of that

* A = 1 Angstrom unit = 10^{-8} cm.

of visible light. These rays are refracted but little when passing from air to a solid medium, the refractive index differing from unity by a very small amount. There does not therefore appear to be any hope of constructing a lens capable of focussing X-rays in the way that light rays can be focussed. X-rays can, in a sense, be focussed by diffraction by a curved crystal, and an attempt has been made to produce images in this way; the instrument has, somewhat optimistically, been called an X-ray microscope. This is a misnomer as it can only produce an image of the same size as the object (magnification unity); nevertheless, it may, in spite of this drawback, find some applications. One field in which the instrument might be used is in the study or detection of segregation in alloys. It produces images the position of which depends on the wavelength of the radiation emitted by the object. If the object consists of strips of two metals A and B, and these are irradiated by an intense beam of X-rays, the characteristic radiation of each metal will be excited. These characteristic radiations are focussed on a photographic plate, but in two separate images, one produced by those parts of the specimen consisting of A, the other by those consisting of B. The segregation is thus recorded, but the lack of magnification sets a limit to the usefulness of the instrument.

The most hopeful direction of advance towards a higher resolving power is by using electrons to form an image of the object under investigation. An electron in motion is accompanied by a wave of very minute length which is diffracted by matter in much the same way as light or X-rays. The wavelength of the electron is equal to Planck's constant, h, divided by the momentum, or, in terms of the accelerating voltage, V, $\lambda = \sqrt{150/V}$. With V = 60,000 volts, the value of λ is 0·05 A, or about 1/100,000 of the wavelength of light. It is probably not possible to make use of electrons scattered through large angles which means that the angle α in (1) is small; but even if $2 \sin \alpha$ is as small as 0·01, the limit of resolution would be 5 A—a distance of atomic dimensions. This resolving power would justify the use of magnifications as large as one million if lenses can be constructed to effect it. The instrument is still in its infancy, but already accounts have appeared of objects photographed at 80,000 magnifications. These high powers have not as yet been applied to the study of metals, but some interesting work at low magnifications has been published on the observation of phase changes (α to γ iron) and the growth of metal crystals at elevated temperatures.[7]

The general features of the instrument are shown diagrammatically herewith, the arrangement being that used for investigation of thin specimens through which the electron beam passes. At the top is a source of electrons, such as a dull emitting cathode, from which the electrons are accelerated by a field of 10 to 70 kV. They then pass through a magnetic "lens" which concentrates the beam on the object. The lens is a coil carrying an electric current and shrouded by iron, except for a narrow ring of non-magnetic material on the inner surface; the coil produces an intense magnetic field symmetrical about the axis of the instrument which focusses the electron beam as light is focussed by a convergent lens. This part of the apparatus is analogous to the source of light and condensing lens used in substage illuminating systems in the optical microscope. The electrons scattered by the object are brought to a focus by the objective lens, and the image so formed undergoes a further stage of magnification by a third lens—the optical equivalent of a projecting lens. The whole system is very similar to optical photo-micrographic equipment. It is, of course, entirely enclosed in an evacuated tube, which has been omitted from the figure for the sake of simplicity. An instrument described by Borries and Ruska[5] has a length of about 1 m. from the condenser to the final image. The objective of focal length, 5·4 mm., produces a magnification of 75 diameters, and the projecting lens, focal length 1 mm., 400 diameters, making a total magnification of 30,000 available. The accelerating voltage used was 80 kV, and the image is recorded directly on a photographic plate placed in the vacuum.

The diagram illustrates the principles employed

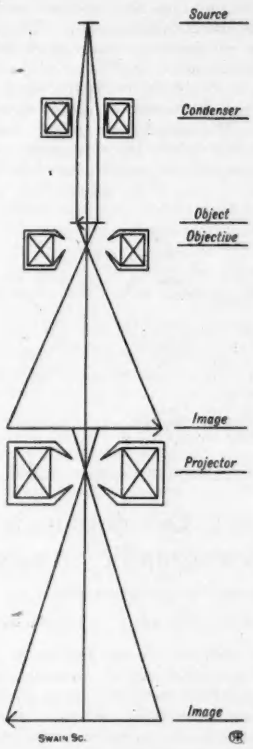


Diagram of the Electron Microscope

for obtaining highly magnified images of semi-transparent objects which have been applied to the investigation of biological material. For the examination of metal surfaces the condensing lens can be dispensed with; the metal is made to emit electrons by depositing on it a thin film of barium and strontium oxides and raising its temperature until it emits as a cathode. The method has the disadvantage of contaminating the surface, but the metal can be examined at temperatures from 700 deg. to 1000 deg. Cent., and phase changes and crystal growth are directly observed. The method is also applied to the study of changes in the emission characteristics of the cathode. For the most part, low magnifica-

tions, of about 100 diameters, are used in this type of work.

The great advantage of the electron microscope is the increased resolving power which it places at our disposal. At the moment, the use of high magnifications for the examination of metals presents difficulties, and, indeed, it may prove to be impossible to realise the high resolution in this field that is available when the specimen is semi-transparent and is examined by transmission. Apart from this, however, the possibility of observing metal surfaces at elevated temperatures is a feature which would seem to have a field of utility.

In a recent review of improvements in the technique of microscopy, Roll,[6] in addition to the matters already referred to above, describes some other interesting appliances. Among these is an instrument for the observation of metals at temperatures up to 1000 deg. Cent. by the optical microscope, at magnifications of 200 diameters. Photographs by Essen of the α–γ transformation in iron and of electrolytic iron containing oxygen, are reproduced. Roll also describes a small accessory for making a determination of the hardness of different constituents of an alloy. The impression of a small diamond pyramid is measured under a magnification of 500; the impressions are so small that hardness figures can be obtained for the different crystals in a specimen with greater certainty, it is claimed, than by the use of a scratch hardness method.

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Recent Developments of Spectrographic Analysis

By E. VAN SOMEREN, B.Sc.

No. II (*continued from April issue*).

THE year 1938 has been fertile in publications dealing with spectrochemical analysis, and all who are interested in this subject will be pleased to learn of steps which have been taken to make it easier to keep abreast of its current developments.

One such step is the publication of two booklets by Adam Hilger, Ltd., dealing with the present state of the subject[1] and with its bibliography from 1933–37[2]. The first of these is such a complete and informative set of abstracts that every spectroscopist should possess it.

Messrs. Julius Springer, of Berlin, published at the beginning of June a work dealing with spectrochemical analysis under the title "Spectrochimica Acta" in a series of booklets which are appearing at first irregularly, later probably at regular intervals. Papers will be printed in either German, English, or French, and a board of three editors, Professor W. Gerlach, Mr. F. Twyman, F.R.S., and Professor R. Breckpot, will be responsible for maintaining the standard of the papers printed. The title of the new periodical gives further recognition to the term spectrochemical analysis which is gradually replacing spectrographic analysis, spectrum analysis, and spectroscopic analysis in order to differentiate this subject more readily from other lines of research, such as the analysis of spectra, the analysis by means of X-ray spectra, and so on.

Developments in the technique of spectrochemical analysis are surveyed in a paper by Professor Gerlach[3] at the annual autumn conference of spectroscopists in Jena in 1938. This discourse is too full of detail to be summarised, and most practising spectroscopists will have read it by now. Of outstanding interest is his mention of the extension of the scope of spectrochemical analysis to sulphur and selenium by a special technique of vacuum spectroscopy developed in the U.S.A. Small traces of sulphur in nickel can be estimated, and the method offers possibility of application to the detection of the poisoning of catalysts by these two elements. German workers have already extended the sensitivity with which phosphorus can be detected in some metals below the limit where its presence can be confirmed by direct chemical means. The use of the spectrograph to verify the purity of reagents which are being used for chemical analysis is urged; in this connection the writer remembers testing the residues from ½ litre each of "pure" nitric acid and ammonia which had been evaporated to dryness, carefully, in a metallurgical laboratory. At least a dozen metals could be detected in each residue—fortunately a quantitative estimation was not required.

In the technique of spectrochemical analysis both arc and spark methods continue to increase their accuracy, and users have almost ceased to advocate one to the exclusion of the other. Considerable electrical research on spark circuits has been carried out in Germany, and although additional elaborations are put forward and are said to give additional accuracy, the fundamental physical problems of spark emission from metal electrodes remain unsolved. Some of the circuits would delight a short-wave wireless engineer more than the average analyst. The ionised interrupted arc associated with the name of Pfeilsticker[4] has been further developed during 1938, and this leads to greater sensitiveness to some elements and spectra with less disturbing background due to the atmosphere. Another modification of the interrupted arc discharge is produced by loading the arc gap with a large capacity and restricting the charging current (at 220 volts), so that it is insufficient to maintain the arc across the gap once the condenser has discharged. This gives very large peak currents unaccompanied by excessive heating of the electrodes, and so is particularly recommended for light alloys and gives very uniform spectra.

A very different general survey, which might be recommended as an introduction to spectrochemical analysis, emerges from the laboratories of the U.S. Navy.[5] In recent years the purchasing and inspection departments of both U.S. and our own navies have been attracted to spectrochemical analysis by the ease with which large numbers of samples can be checked to specification. In the American publication few technical details are given (by comparison with the German standards), but the range of materials dealt with is described—steel, aluminium alloys and lead were the first subjects chosen.

Another general paper on the scope of spectrochemical methods comes from the laboratories of the Robert Bosch G.m.b.H., of Stuttgart,[6] which illustrates graphically a number of typical problems and a few unusual ones. One of these is the evidence

that an engine has been used with leaded fuel which can be obtained by the spectrochemical examination of the sparking plug points, which, when sparked in front of the spectrograph, will show lead. The detection of phosphorus in lubrication oil, which was afterwards found to contain tricresyl phosphate, is an odd engineering application, while a more subtle one is the detection of fluorides in the protective coating on elektron metal. Although fluorine has no distinctive spectrum, calcium fluoride has a band spectrum in the ultra-violet which affords a very sensitive test for this substance, and by chalking the protective coating on the metal before sparking it was proved that some coating treatment had been used which deposited fluorine compounds.

An attempt was made at Jena by one of the pioneers of spectrochemical analysis, Professor Lundegardh, of Uppsala, to reintroduce to metallurgical analysts the old flame test with a new technique.[7] If an oxy-acetylene flame is used as a light source for a spectrograph, some two dozen elements can be made to give their spectra. By passing a spark through the flame the extra energy input extends the scope of the method, so that forty-five elements can be caused to emit in this way. Although the light from the spark gap in the flame is being examined, the material under test is not used as an electrode, but is introduced into the gas fed to the flame by means of an atomiser of the "scent-spray" type made of platinum-iridium alloy and arranged in a glass bulb in the gas stream.

The advantages of this method to the metallurgist are limited to special cases. One advantage only arises when alloys of marked inhomogeneity are being tested, as then a solution of the sample must be made unless the spectrograph is being used to detect the heterogeneity as well as the minor constituents. If a solution is to be used it is easier to regulate the way in which it is sprayed into a flame than to control the amount used when introduced into a spark or arc. In each case the use of solutions raises problems of cleanliness and adsorption on glass and accidental contamination which the spectroscopist probably hopes he had left to the chemist when he changed over to physics—but such problems are raised only to be solved, and the claim for this method is that higher accuracy which can be obtained in routine quantitative testing when the spark in a flame is compared with the spark between solid electrodes. Problems of background to the spectrum make this method unsuitable for a few metals, but it is said to be particularly applicable to the estimation of the main constituents of alloys where direct spark spectrochemical analysis is not quite accurate enough. The writer is of the opinion that it might well be applied to light alloys in general, unless silicon is to be estimated.

A very detailed investigation of one of the factors which complicate the spectrochemical analysis of light alloys comes from G. Balz,[8] who has investigated the effect of zinc on the determination of magnesium in aluminium alloys. It was found that the presence of 10 per cent. of zinc made the alloys appear much too rich in magnesium if sparked directly, but that sparking solutions eliminated this effect. The extension of quantitative spectrochemical analysis to higher concentrations depends on the possibility of avoiding complications of this kind, and the use of solutions is sometimes necessary in order to obtain greater uniformity of the light source than can be obtained from varying alloys sparked under the same electrical conditions. In Professor Lundegardh's method it is sometimes found advantageous to introduce a known uniform quantity of a sodium salt into all the solutions being analysed so as to level out the effective conductivity of the spark gap in the flame by providing plenty of easily ionised atoms.

From Copenhagen comes an account of detective work in which the spectrograph has played an essential part. Two papers by Dr. Paul Bergsoe[9] published in English recount a most ingenious attempt to reconstruct the metallurgical methods of the pre-Columbian Indians of Ecuador. These people found native gold, platinum, and copper, and became jewellers with a cult of small-scale craftsmanship; they seem to have worked without furnaces or crucibles, using blow-pipes, welding, and forging to produce not only precious metal objects, but also gilded copper ones. Spectrochemical analysis was used to compare different copper objects and to prove that mercury amalgam was not used for gilding, as had been suggested by previous archæologists. These papers can be recommended to metallurgists who welcome a closely knit argument, and to museums whose authorities are content to remain ignorant of the identity of many of their specimens on the old-fashioned ground that they are too precious to analyse—the spectrograph destroys that plea nowadays.

Returning from the application of spectro-chemical analysis to its details, a further study of sources of error in quantitative analysis comes from Werner and Rudolph.[10] Some of the examples given are rather obvious, but it is instructive to find them so clearly explained and illustrated by quantitative data taken from the analysis of lead by spark methods. The unusual feature of this paper is that the effect of the variation of contrast factor of the photographic plate for decreasing wavelength is dealt with adequately, data are given for two typical plates, and the authors point out that by selecting a suitable plate this source of error can often be eliminated, even where it is necessary to make intensity comparisons between two widely separated lines.

From the Vatican, or, rather, from the astrophysical laboratory of the Vatican Observatory, a series of papers have been published of special interest to ferrous metallurgists. It is not generally known that the astronomical work of this Observatory is supplemented by an astrophysical department in which stellar spectra and meteoric samples can be analysed. The German workers in this laboratory have produced charts of the arc and spark spectra of iron based on photographs of very high dispersion, and also a study of the preparation of pure iron.[11] After a detailed comparison of the purest iron available from British and European sources,[12] they remain unsatisfied that at least five elements cut them off from perfection, and they have developed a method of making pure iron without elaborate chemical manipulations. The solubility of ferric chloride in ether is made the means of eliminating all other metallic impurities, and the reduction of the chloride to metal, which they used in the form of a sintered powder, can be accomplished without metallic contamination. Manganese and occasionally copper may still be detected by the spectrograph in the resulting metal; carbon and oxygen are probably also present.

Another paper[13] from the same laboratory describes the quantitative estimation of carbon in steel spectrochemically. This is of minor interest, as the line used is not separated from an adjacent iron line by

many spectrographs, and is masked by nickel and other alloying elements.

An American thesis dealing with arc welding[14] describes the use of spectrochemical analysis to estimate the varying distribution of manganese in different regions of the weld metal deposited in a steel rail joint. This is an instance where a large number of tests were made rapidly by using sparks at definitely localised regions on the sample, eliminating the necessity for cutting it up and dealing with a large number of small samples.

Some of the more difficult analyses in alloy steels, such as that for vanadium,[15] tantalum and niobium,[3] are now being carried out spectrochemically, and the rapid qualitative identification of all the elements in a steel sample is still a task which a chemist should be glad to leave to a spectroscopist.

For assistance in this task one may turn to the tables recently produced in Germany[16] of lines which can be used for the identification of sixteen possible alloying elements in steel. This work was done with a spectrograph of the smallest dispersion which is ever used for steel, and consequently its information about disturbing lines which can make the identification more difficult errs on the side of caution. The paper is illustrated by good enlargements, and contains some data on quantitative comparisons. A guide to qualitative analysis in the form of a series of charts of spectra with the iron arc as a reference spectrum has recently been produced in Chicago.[17] The charts were drawn from spectra photographed with a high dispersion, and are intended to be used on the screen of a spectrum projection apparatus whose magnification can be so adjusted as to make part of an iron arc spectrum on the plate fit the iron arc lines on the chart.

An attempt is made in a characteristically German paper by Thanheiser and Heyes[18] to measure statistically the accuracy with which some elements can be estimated in steel and weigh the errors introduced by such obvious mistakes as using a thin wire or a large chunk of metal instead of a rod as each electrode, or by selecting unsuitable lines for comparison. Five pages of text and nine of tables are provided to prove that the rules made after a few empirical trials by pioneer workers from five to ten years ago are still worth keeping.

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Embrittlement of Creep-Resisting Steels at High Temperatures

THE increased use during the last ten years of steels under conditions of service in which they are exposed to high temperatures and pressures has led to the recognition of the phenomenon of "long-time embrittlement" or the production of a notch-brittle condition by prolonged exposure to

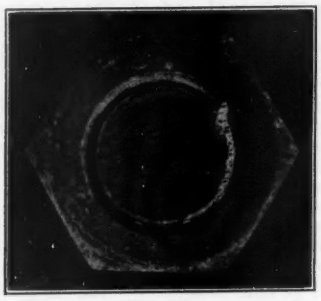


FIG. 1—*Brittle Fracture of a Nickel-Chromium-Molybdenum Steel Bolt*

the working temperature. In a recent number of *Archiv*, R. Scherer and H. Kiessler* review this question in the light of published information and of the results of their own preliminary investigations. The paper contains a list of more than twenty references. These will not be reproduced here, nor will much reference be made to work already published in English, although the authors devote considerable

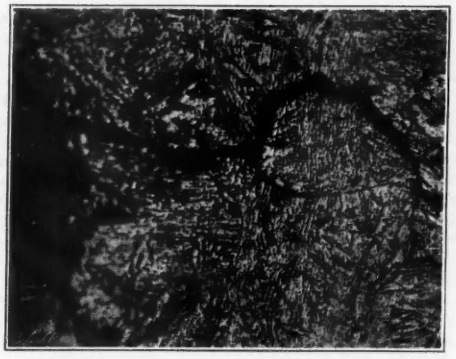


FIG. 2—*Microstructure of the Steel Adjacent to the Fracture*

attention to it. There are only a few German publications dealing with the brittle fracture of creep-resisting steels. The authors illustrate the phenomenon by Figs. 1 and 2, which show the appearance of the fracture of a screw bolt which has been subject

* *Archiv für das Eisenhüttenwesen*, February, 1939, 1938/39, 12, 381.

to long exposure at high temperature and the adjacent microstructure revealing intercrystalline cracks. E. Houdremont, the first German worker in this field, concluded from an examination of broken ends of bolts, which he found to possess the usual strength and toughness values, that general embrittlement did not occur. He also carried out tests, on notched specimens, of "time-to-fracture" under different loads. (*Zeitstandfestigkeit*). These times were found

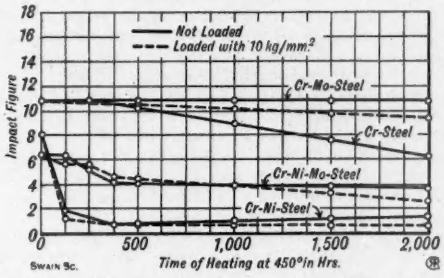


FIG. 3—*Effect of Heating at 450 deg. Cent. on Impact Figure at Room Temperature (Michailow-Michejew)*

by E. Siebel to be much lower than the endurance of a standard creep specimen for nickel-chromium-molybdenum steel, but the two were found to agree approximately for chromium-molybdenum steels. F. Kaissling associated the embrittlement with strain ageing, and recommended the use of non-ageing materials. E. Reinicke reported in contradiction to the findings of Houdremont, that broken bolts showed embrittlement throughout, and W. Buchmann found very low impact values in the majority of broken bolts of the approximate composition, nickel 1·5, chromium 1·0, molybdenum 0·9 per cent. W. Ruttmann believed that all steels with high creep endurance tend to give fracture without deformation, and recommended lowering of stresses and use of steels of lower strength.

All these opinions were expressed after 1936, and their diversity is perhaps surprising in view of the work of R. W. Bailey in 1928 on the premature failure of creep-resisting steels embrittled by long exposure to high temperatures. Since then many investigations have been carried out, chiefly on the plan that materials of different compositions were heated for long times at temperatures between 350 deg. and 550 deg. Cent., with or without loading,

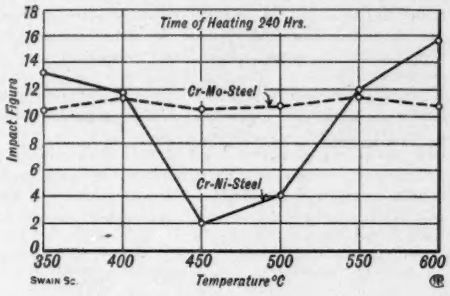
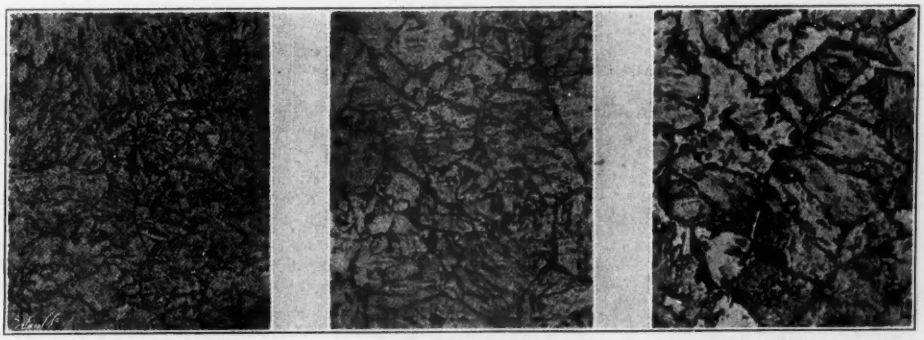


FIG. 4—*Effect of Heating for 240 Hours at Temperatures between 350 deg. and 600 deg. Cent. on Impact Figure at Room Temperature (Michailow-Michejew)*

and the impact figures, measured at room temperature, compared with the initial values. Experience has shown that materials which exhibit a marked fall of impact figure in such a test are liable in practice to brittle fracture. P. B. Michailow-Michejew (1936) obtained the results shown in Figs. 3 and 4. The fall of impact figure was greatest and most rapid in nickel-chromium steel; smaller and slower in nickel-chromium-molybdenum steel; very gradual in chromium steel, whereas in chromium-molybdenum steel the impact figure was almost unchanged after 2000 hours' heating at 450 deg. Cent. Loading of the specimens had no considerable effect. Fig. 4 shows the detrimental effect of exposure to temperatures of 450–500 deg. Cent. on nickel-chromium steel, while chromium-molybdenum steel shows no



FIGS. 5 TO 7—*Change in Structure of Nickel-Chromium-Molybdenum Steel After 7000 Hours' Exposure to Working Temperatures of 460 deg. and 490 deg. Cent. (Etched with Nitric Acid ×500)*

FIG. 5—*Initial Structure* **FIG. 6**—*Same Steel After Use at 460 deg. Cent.* **FIG. 7**—*Similar Steel After Use at 490 deg. Cent.*

alteration of impact figure over the whole range 350–600 deg. Cent.

These results are in general agreement with those of several English investigators, but it may be noted that T. Swinden has found that there is a tendency for the impact figure of some steels to rise again after more than 2000 hours' exposure, *i.e.*, beyond the maximum time employed by Michailow-Michejew. There is not general agreement as to whether loading accelerates, or is without effect on, the fall of impact value; but since the embrittlement can take place without any loading or deformation, strain ageing does not enter into the question. Without offering any precise explanation of the phenomenon, most investigators assume that the cause of long-time embrittlement is the same as that of temper brittleness.

In order to assess the effect of composition on embrittlement, Scherer and Kiessler examined the records of eighty different steels and state that they only occasionally encountered contradictions. Their classification is as follows :—

Strong tendency to embrittlement—nickel-chromium, manganese, and copper steels.

Fairly strong tendency to embrittlement—chromium-silicon, and nickel steel.

Small fall in impact figure—carbon steels, chromium, and molybdenum steels, and those with the following combinations :—Chromium-tungsten, manganese-molybdenum, nickel-molybdenum, nickel-chromium-molybdenum, chromium-silicon-molybdenum.

Almost free from embrittlement—chromium-molybdenum steels.

This classification, though stated to be subject to exceptions, was found to hold with sufficient certainty for the authors to base on it a recommendation that structures should be designed for lower stresses and use made of nickel-free steels, especially chromium-molybdenum steel.

Scherer and Kiessler then proceed to describe their own preliminary experiments on embrittlement by long heating. After 1000 hours at 500 deg. Cent. they found no fall in impact figure of chromium-molybdenum steels, but a distinct fall in similar steels containing nickel or silicon.

Some typical compositions involved were :

	C.	Cr.	Mo.	Ni.	Si.
A	0·12 ...	0·80 ...	1·04 ...	1·62 ...	—
B	0·17 ...	1·36 ...	1·38 ...	— ...	1·25
C	0·30 ...	1·46 ...	1·35 ...	— ...	—
D	0·12 ...	0·87 ...	0·81 ...	— ...	—

A and B showing a fall, C and D a rise in impact figure.

The "time-to-fracture" of notched specimens of steels, all having the same creep strength, varied considerably, again in favour of the chromium-molybdenum steel B (or a similar steel containing tungsten and vanadium in place of some of the molybdenum) over the nickel-chromium-molybdenum steel A. Screw bolts of nickel-chromium-molybdenum steels which had been in use for several thousand hours occasionally broke at their most highly stressed point. Tensile test pieces cut from them gave no significant change in properties, but notched bar impact values had fallen from 20 mkg. to 3–6 mkg. per square centimetre. The fall was no more pronounced in highly stressed regions than in the other parts of the bolts. A definite change in microstructure, consisting of intensification of the grain boundaries of sections etched in the usual way with nitric acid was reported (Figs. 5–7). Sodium picrate and Murakami's reagent revealed no difference between the tough and brittle condition, so it is not yet known with certainty what change in the structure of the grain boundaries occurs. In associated work by G. Riedrich (shortly to be published) a portion of an embrittled bolt was heated for ten hours at 610 deg. Cent. The impact figure of 3·4 mkg. per square centimetre jumped to 22 mkg. per square centimetre, with a simultaneous fall of tensile strength from 85 kilos. to 70 kilos. per square millimetre. It was found that heating for one hour at the same temperature produced a similar rise of impact figure without appreciable loss of tensile strength. A portion of the embrittled bolt was therefore heated for one hour at temperatures between 500 deg. and 600 deg. Cent., a region lying between the working temperature of 460 deg. and the original tempering temperature of 630 deg. Cent. The impact figure rose, at first slowly, and then, above 560 deg. Cent., rapidly to 20 mkg. per square centimetre after treatment at 600 deg. Cent. The change in tensile strength was extremely small; as calculated from the Brinell hardness it rose from 87 kilos. to 90 kilos. per square millimetre, and then fell again to 86 kilos. per square millimetre. Thus, by reheating at a suitable temperature between the working temperature of the bolt and the original tempering temperature of the steel, the embrittlement can be largely removed, though a material restored in this way would be freshly embrittled by renewed exposure to the working temperature. An exactly similar behaviour to the above is shown by temper-brittle steel.

On the basis of their examination of published information and on the results of their own preliminary experiments, Scherer and Kiessler put forward the following ideas about the embrittlement and failure produced by prolonged exposure to high temperatures :—

(1) The cause of the fracture without deformation is a general embrittlement of the material coupled with the presence of localised high stress.

(2) The long-time embrittlement is attended by a strong intensification of the grain boundaries in the etched section.

(3) Long-time embrittlement is identical with temper brittleness and has nothing in common with strain-ageing embrittlement.

(4) Embrittlement by prolonged exposure to high temperatures can, in practice, be avoided by the use of nickel-free steels the composition of which is so chosen that the structural alteration to the grain boundaries is largely suppressed.